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DISSOCIATION REACTION OF MAGNESIUM CARBONATE

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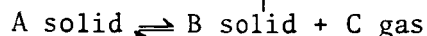
RATE OF NUCLEATION OF THE NEW SOLID PHASE IN THE THERMAL
DISSOCIATION REACTION OF MAGNESIUM CARBONATE

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ABSTRACT: A mechanism presented in an earlier work outlining the stages in nucleation reactions, e.g. the formation of CaCO_3 from CaO and CO_2 , is used as a basis for calculations of the kinetics and reaction rate in such reactions. A formula expressing the relationship between the log of the nucleation rate and the inverse square log of the supersaturation is presented, then applied to the results of earlier experiments on the decomposition kinetics of CaCO_2 and the reverse reaction. The points on a graph of $\log J'$ vs. $1/\log^2(p/p_0)$ fall on a straight line.

Using the results of earlier studies of reactions of thermal dissociation and reactions proceeding in the reverse direction, one of us [1-3] has proposed a hypothetical mechanism for the process of nucleation in reactions of the type



In accordance with these hypotheses, the nucleation of the new solid phase, for example, in the case of formation of CaCO_3 from CaO and CO_2 , takes place in the following stages:

- a) Adsorption of CO_2 molecules on the CaO surface, two-dimensional diffusion over the surface to active sites where the chemisorption of CO_2 takes place;
- b) Penetration of chemisorbed CO_2 molecules into the surface layers of the CaO crystal lattice, in which the arrangement of the atoms undergoes deformation as a result of chemisorption. This gives rise to microdefects in the lattice.
- c) Surface concentration of microdefects due to the mobility in certain areas on the surface, i.e., sites of damage, corners, crystal edges, etc.;
- d) Transformation of the CaO lattice into a CaCO_3 lattice at points

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* Numbers in the margin indicate pagination in the foreign text.

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where a sufficient number of microdefects have accumulated, so that the newly formed CaCO_3 nucleus is stable.

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e) Growth of the CaCO_3 nucleus formed (as a result of the reaction taking place at the interface of the substrate phase and product) up to the time when, as a result of stresses arising on the solid phase interface due to differences in the dimensions of the unit cells of the lattice and differences in the type of lattice, the small crystal of product formed becomes detached from the surface of the substrate. Simultaneously with the detachment of the crystal from the substrate lattice, the crystal ceases to act as a nucleus, and the process of nucleation must be started over again.

The adoption of the above mechanism became the basis for deriving a general relationship for the nucleation kinetics in the reaction of thermal dissociation and the reverse reaction. Extensive studies of the kinetics of these processes showed that depending on the degree of supersaturation, the process can have two different courses. In the range of low supersaturations, the reaction rate v varies linearly with the distance of the system from the state of equilibrium ($p - p_0$):

$$v = k(p - p_0) \quad (1)$$

where k is a constant, p is the pressure of the gaseous reactant in the reacting system, and p_0 is the decomposition pressure at the temperature of the experiment.

In the range of high supersaturations, the reaction takes place primarily as a result of formation of nuclei of the new solid phase in accordance with the mechanism given above. On the basis of the assumptions contained in this mechanism and the Langmuir theory, the following dependence was derived [2], [3]

$$J' = \frac{k_0}{\Phi} - 1 \quad (2)$$

with

$$\Phi = \frac{\left(\frac{p}{p_0} - 1\right)}{v} \text{ for } p \gg p_0 \quad (3)$$

and

$$\Phi = \frac{\left(1 - \frac{p}{p_0}\right)}{v} \text{ for } p \ll p_0 \quad (4)$$

where J' is a quantity proportional to the nucleation rate I , and k_0 is the constant from equation (1) in the vicinity of the state of equilibrium.*

On the basis of general equations of the theory of nucleation, the following relation was found:

$$\lg J' = -A \frac{1}{\lg^2(p/p_0)} \quad (5)$$

This relation expresses the existence of a simple proportion between the log of the nucleation rate and the inverse square of the log of the supersaturation.

The relation derived was applied to calculations of results of earlier experiments on the decomposition kinetics of calcium carbonate and the reverse reaction, i.e., the action of carbon dioxide on calcium oxide. It was found that on graphs of $\lg J'$ vs. $1/\lg^2(p/p_0)$, the points corresponding to individual measurements of the given experiment fall on straight lines. This fact constitutes a confirmation of the validity of the derived formula and of the assumptions inherent in the adopted mechanism of formation of the new solid phase. It was also found that the undoubtedly complex phenomenon of nucleation involving a simultaneous transformation of the crystal lattices takes place in accordance with the same laws governing simple processes of nucleation during condensation, boiling and crystallization.

$\lg J'$ vs. $1/\lg^2(p/p_0)$ is different depending on the properties of the reacting solid phases, which are characterized by coefficient A of Formula (5).**

Experimental

Scope of the Investigations and the Experimental Method Employed.

Studies recently undertaken on the thermal decomposition of magnesium carbonate were aimed at collecting experimental material on the $MgO-CO_2$ system and checking the above conclusions concerning the reaction rate in the range of high supersaturations, where the process takes place mainly as a result of the nucleation of the new solid phase.

The following substances were used in the studies: 1) magnesium carbonate prepared by drying basic magnesium carbonate in a stream of CO_2 at 340° [5], 2) magnesium carbonate prepared by Potapenko's pressure method [4] from a solution of $MgCl_2$ and $NaHCO_3$. Both preparations were subjected to

* In ref. [2], ϕ was erroneously calculated for $p < p_0$ according to relation (3).

** Translator's note: Seems to be out of context in the original Polish.

a final dehydration in the apparatus used for the measurement in question.

For the purpose of a preliminary determination of the dissociation temperature, magnesium carbonate prepared by Potapenko's method was analyzed thermogravimetrically in a device constructed at the Department of Technological Planning of the Warsaw Polytechnic School [6]. According to Tsvetkov [7], in the case of pure anhydrous magnesite, the curve of heat effects shows only one extremum corresponding to dissociation at about 600° and associated with a substantial weight loss.

Thermogravimetric analysis of the preparation used in further kinetic measurements (Fig. 1) showed that the dissociation temperature for this preparation is about 620°. The determination of this temperature facilitated the selection of appropriate conditions of measurements of the reaction rate in further investigations.

Experiments on the kinetics of thermal dissociation of magnesium carbonate were carried out in a static apparatus by determining the rate of discharge of carbon dioxide through the system.

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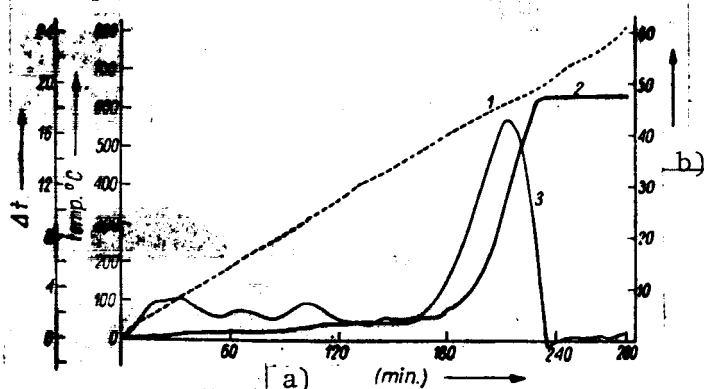


Fig. 1. Thermogram of Magnesium Carbonate. Curves: 1, Change of Temperature of Sample; 2, Change of Weight of Sample; 3, Differential Thermal Analysis; a, Time (Min.); b, Change of Weight.

with the vacuum pump system (rotary oil pump, preliminary vacuum tank and mercury diffusion pump). The temperature of the preparation was measured with a Pt/PtRh thermocouple. The reaction vessel was placed in an electric resistance furnace in which the constant temperature zone had been previously determined. The temperature during the experiment was kept constant by automatic control of the heating of the furnace with the aid of an Ortex two-position thermoregulator governed by a Pt/PtRh thermocouple placed outside the retort.

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After pressing, the preparation studied was ground to a grain size of 0.8-1.5 mm and placed in a quartz retort (Fig. 2). A quartz tube connected to this retort, which constituted the reaction vessel (in which the quartz housing of the thermocouples is placed), formed the reaction zone together with two mercury manometers. A flow-through stopcock connected this part of the apparatus with the vessels, i.e., the vacuum tanks, with manometers for measuring the pressure in these tanks and

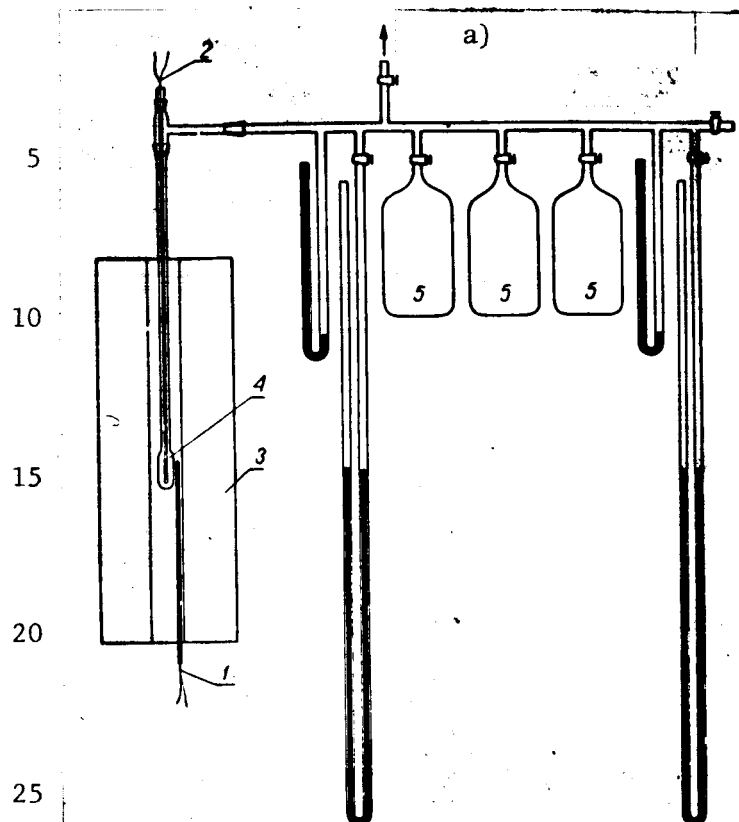


Fig. 2. 1 and 2, Thermocouple; 3, Tubular Resistance Furnace; 4, Reaction Vessel; 5, Vacuum Tank; a, To Vacuum Pump System.

Results

Serious difficulties were encountered in attempts to determine the decomposition pressures of magnesium carbonate. The system studied behaved in an irreversible manner, showing an immeasurably slow course of the reaction opposite to the thermal dissociation reaction. In the course of the experiments, processes of physical adsorption and desorption of CO_2 were observed to take place over a very wide temperature range. The occurrence of these processes considerably complicates the study of the thermal dissociation of magnesium carbonate.

The results of the measurements were collected in Tables 1-2, which give the average pressure in the course of the measurement and the reaction rate expressed in terms of the rate of change of pressure in mm Hg/min. The value of this rate is of course characteristic only of the given series of measurements, since it depends on the size of the charge, its composition, the size of the gaseous space, etc.

The largest possible loads and a small gas space of the apparatus were used in order to eliminate the effect of a change in the composition of the solid phases on the reaction rate. After a pressure markedly different from the equilibrium pressure had built up above the system, the reaction rate was determined by measuring the rate of changes in the gas pressure over the system. To this end, a stopwatch was used to determine the time in which the mercury column in the manometer indicating the pressure in the system shifted between two marks on a magnifying glass through which mercury level in the manometer was observed.

In the experiments discussed, the magnesium carbonate charge amounted to about 5 g, and the shift of the mercury column between the marks of the magnifying glass corresponded to a 0.1% change in the composition of the solid phase.

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TABLE I *

Preparation 1.

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Experiment
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p	v	p/p_0'	$\Phi \cdot 10^4$	$J' \cdot 10^3$	$\log(J' \cdot 10^3)$	$1/\log^2(p/p_0')$
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1	$t = 386^\circ\text{C}$	$p_0' = 240 \text{ mm Hg}$		$k_0' \cdot 10^3 = 118$		
47	10,8	0,1911	4,127	186,2	2,2700	1,935
63	9,85	0,2561	7,552	56,2	1,7497	2,857
79	6,52	0,3211	10,41	13,3	1,1239	4,108
2	$t = 386^\circ\text{C}$	$p_0' = 289 \text{ mm Hg}$		$k_0' \cdot 10^3 = 163$		
46	10,8	0,1710	7,676	112,4	2,0507	1,700
63	5,8	0,2342	13,20	23,5	1,3711	2,516
95	4,02	0,3532	16,09	1,30	0,1139	4,895
3	$t = 391^\circ\text{C}$	$p_0' = 195 \text{ mm Hg}$		$k_0' \cdot 10^3 = 140,5$		
43	15,00	0,2205	4,997	181,2	2,2582	2,320
61	6,64	0,3128	10,35	35,7	1,5527	3,926
77	4,44	0,3949	13,63	3,08	0,4886	6,142

(4")

A graph of the function $v = f(p)$ showed the curves obtained to be similar to analogous curves for experiments in which apparent equilibria take place.

In earlier studies it was shown that when apparent equilibrium pressures p_0' arise in a system, p_0' should be introduced into equation (1) instead of p_0 . For this reason, in our further reasoning, the degree of supersaturation taken was the ratio of the pressure of carbon dioxide in the system at a given instant to the apparent decomposition pressure of the system at the temperature of the measurement.

For each experiment, the apparent equilibrium pressure p_0' characterizing the state of the surface was determined graphically from a plot of the function $v = f(p)$. This was done because these plots gave curves which showed a rectilinear course in all cases over a certain range. This rectilinear course probably corresponds to the kinetic range at small distances from the apparent equilibrium. With this assumption, extrapolation of this segment to the intersection with the pressure axis made it possible to determine the apparent equilibrium pressure p_0' of a given experiment. The slope of this curve then corresponds to constant k' from the modified formula for the reaction rate:

*Tr. Note: Commas indicate decimal points.

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TABLE II *
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Preparation 2.

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Experiment
Number

	p	v	p/p_0	$\Phi \cdot 10^3$	$J' \cdot 10^3$	$\log(J' \cdot 10^3) 1/\log^2(p/p_0)$
4	$t=495^\circ\text{C}$		$p_0=129$	$k_0=453 \cdot 10^{-3}$		
	8	6,48	0,0620	14,48	212,8	2,3279
	13	5,21	0,1008	17,26	162,4	2,2108
	18	3,17	0,1395	27,14	66,9	1,8254
	24	2,14	0,1860	38,04	19,1	1,2810
	30	1,85	0,2326	41,48	9,21	0,9643
5	$t=494^\circ\text{C}$		$p_0=129$	$k_0=453 \cdot 10^{-3}$		
	10	6,86	0,0775	13,45	236,8	2,3744
	16	5,15	0,1240	17,01	166,3	2,2209
	22	3,38	0,1705	24,54	84,60	1,9274
	28	2,58	0,2170	30,35	49,26	1,6925
						2,272
6	$t=498,5^\circ\text{C}$		$p_0=153$	$k_0=281,6 \cdot 10^{-3}$		
	8	12,99	0,0523	7,30	285,7	2,4559
	16	7,59	0,1046	11,80	138,6	2,1418
	22	5,23	0,1438	16,36	72,1	1,8579
	28	4,20	0,1830	19,45	44,78	1,6511
	34	3,41	0,2222	22,81	23,45	1,3701
	40	2,81	0,2614	26,28	7,15	0,8543
7	$t=498,5^\circ\text{C}$		$p_0=148$	$k_0=287,5 \cdot 10^{-3}$		
	8	10,76	0,0541	8,79	227,1	2,3562
	14	6,67	0,0946	13,57	111,9	2,0487
	20	5,43	0,1351	15,93	80,47	1,9057
	26	4,40	0,1757	18,73	53,50	1,7284
	32	3,45	0,2162	22,72	26,54	1,4239
	38	3,02	0,2568	24,60	16,87	1,2271
8	$t=493,5^\circ\text{C}$		$p_0=105 \text{ mm Hg}$	$k_0 \cdot 10^3=372$		
	8	6,99	0,0762	13,22	181,4	2,2586
	14	4,44	0,1333	19,51	90,67	1,9574
	20	3,53	0,1905	22,93	62,23	1,7940
	26	2,38	0,2476	31,61	17,68	1,2475
	32	2,02	0,3048	34,42	8,08	0,9074

* Tr. Note: Commas indicate decimal points.

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Table II [Continued] *
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Experiment
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p	v	p/p_0'	$\Phi \cdot 10^2$	$J' \cdot 10^2$	$\log(J' \cdot 10^2) / \log^2(p/p_0')$	
$t = 498^\circ\text{C}$		$p_0' = 110 \text{ mm Hg}$		$k_0' \cdot 10^3 = 229,6$		
8	11,33	0,0727	8,18	180,7	2,2569	0,7715
14	8,28	0,1273	10,54	117,8	2,0712	1,248
20	6,01	0,1818	13,61	68,70	1,8370	1,824
26	4,10	0,2364	18,62	23,30	1,3674	2,548
32	3,72	0,2909	19,06	20,46	1,3109	3,477
38	2,93	0,3455	22,33	2,82	0,4502	4,692

$t = 498^\circ\text{C}$		$p_0' = 145 \text{ mm Hg}$		$k_0' \cdot 10^3 = 289,8$		
8	11,23	0,0552	8,41	244,6	2,3885	0,6319
14	6,95	0,0965	13,00	122,9	2,0895	0,9699
20	5,12	0,1379	16,84	72,09	1,8578	1,351
26	4,03	0,1793	20,36	42,34	1,6267	1,795
32	3,33	0,2207	23,40	23,85	1,3775	2,322
38	2,78	0,2621	26,54	9,19	0,9633	2,958

$t = 498^\circ\text{C}$		$p_0' = 134 \text{ mm Hg}$		$k_0' \cdot 10^3 = 276,4$		
8	10,44	0,0597	9,01	206,8	2,3156	0,6675
14	7,59	0,1045	11,80	134,2	2,1277	1,039
20	5,71	0,1492	14,90	85,50	1,9320	1,465
26	4,09	0,1940	19,70	40,30	1,6053	1,972
32	3,75	0,2388	20,30	36,16	1,5582	2,585
38	3,06	0,2836	23,41	18,67	1,2500	3,339

$$v = k'(p_0' - p) \quad (6)$$

Values of p_0' and k' thus obtained would then apply in further calculations of the rate of nucleation of the new solid phase.

Figure 3 shows the method of graphical determination of the values of p_0' .

The results of certain measurements were recalculated in accordance with formulas (2) and (4) and collected in Tables 1-2 by giving the following quantities:

t - temperature at which the experiment was carried out,

*Tr. Note: Commas indicate decimal points.

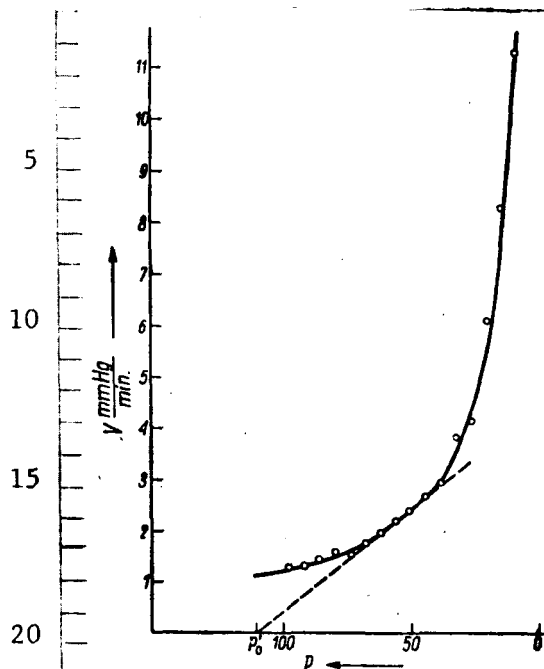


Fig. 3

p_0' - apparent equilibrium pressure, k_0 - value of the reaction rate constant in the vicinity of the state of apparent equilibrium, p - average pressure in the system during the measurement, v - reaction rate expressed as the rate of change of pressure in mm Hg/min, p/p_0' - degree of supersaturation characterizing the distance from the state of apparent equilibrium,

$$\Phi = \frac{1 - p/p_0'}{V} \text{ and } J' = \left(\frac{k_0}{\Phi} - 1 \right),$$

J' - quantity proportional to the rate of nucleation.

These results are also shown in Figs. 4-6 as dependences of $\log J'$ on the inverse square of the log of the supersaturation.

Discussion of Results and Conclusions

The results of the study of the kinetics of magnesium carbonate decomposition (a process which was found to involve apparent equilibria)

confirmed the existence of a simple proportion between the log of the nucleation rate and the inverse square of the log of the supersaturation.

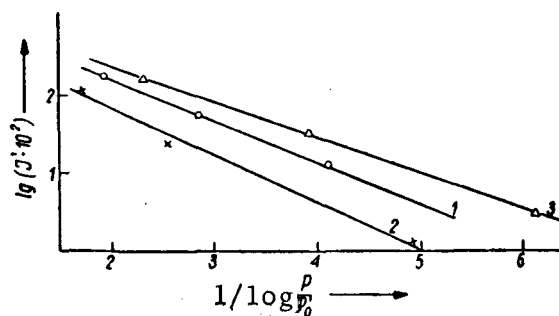


Fig. 4

Deviations of the points corresponding to certain measurements from straight lines are occasionally substantial. It should be noted, however, that values of the apparent equilibrium pressures were introduced into the calculations instead of the equilibrium pressures. The values of p_0' were found

graphically by extrapolating the linear segment of the curves representing the dependence of the reaction rate on the distance from equilibrium, and this undoubtedly decreases the accuracy of these calculations. The results

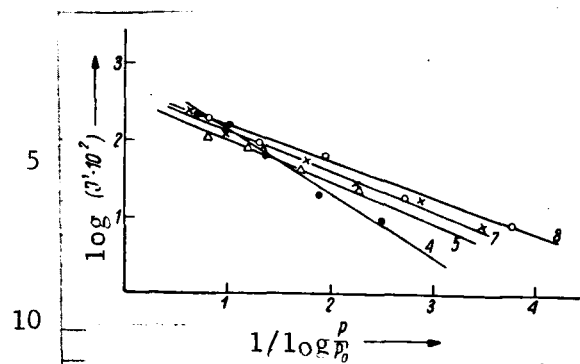


Fig. 5

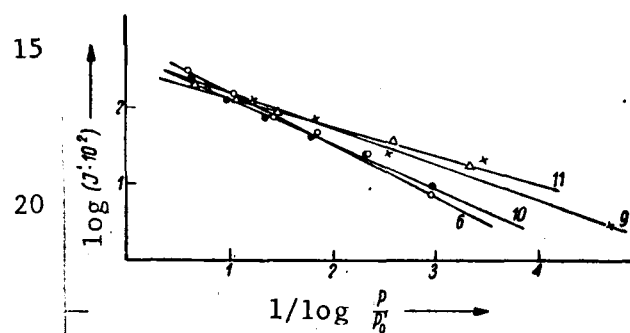


Fig. 6

of the experiments described indicate a general character of the dependence of the nucleation rate on the log of the saturation.

The values of nucleation rates calculated on the basis of experiments carried out at the same temperature and in neighboring pressure ranges differ. As was already noted in earlier studies, this rate depends, among other things, on the way of handling the system before starting the kinetic measurement and on the degree of transformation of the preparation.

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